Advanced class - NMR

Q1. Advanced physical chemistry 1998, Q1

a) Modern NMR spectrometers operate in a *pulsed mode*, where spectra are obtained by *Fourier transformation* of a signal from *free induction decay*. Explain clearly what is meant by the statement with particular attention to the italicised terms. Explain also why it is advantageous to record NMR spectra in a pulsed rather than a continuous mode.

b) Give an account of the factors that make some nuclei more suitable than others for use in NMR.

EITHER explain why ^{13}C lines from atoms adjacent to the halogen atoms Cl, Br and I are affected in frequency but not split by spin-spin coupling, although all common isotopes of these halogens have non-zero nuclear spin.

OR Explain why the ^{1}H spectrum of ammonium salts shows splitting into three lines by the ^{14}N nucleus, but spectra of primary amines show no such splitting of lines for protons bonded to the nitrogen atoms.

c) Distinguish between spin-lattice and spin-spin relaxation in NMR. How can the spin-lattice relaxation time be measured?

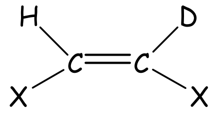
Explain why the 13C nuclear relaxation time for quaternary carbon atoms is much longer than that for carbon in –CH= groups, which in turn is roughly twice as long as in $-CH_2-$ groups. Explain also why the relaxation time for the carbon in methyl groups is relatively long and does not fit into this sequence.

Q2. Advanced physical chemistry 1999, Q1

The nuclear spin energy levels (expressed as frequencies) of molecule 1 in a magnetic field are as follows:

	m_H	m_D	freq / Hz
1	-1/2	-1	+261 457 945
2	-1/2	0	+200 000 000
3	-1/2	+1	+138 542 055
4	+1/2	-1	-138 542 057
5	+1/2	0	-200 000 000
6	+1/2	+1	-261 457 943

You may assume that both carbons are ^{12}C and that X is non-magnetic. D denotes deuterium.



molecule 1

a) Explain the significance of the symbols m_H and m_D, and state the appropriate NMR selection rules.

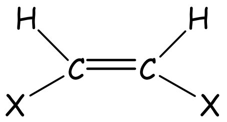
b) By calculating the frequencies of the allowed transitions determine:

i) the H-D spin-spin coupling constant;
ii) γ_H/γ_D, the ratio of the gyromagnetic ratios of the two isotopes;
iii) the strength of the magnetic field in Tesla ($\gamma_H = 2.675\times10^8$ T^{-1}s^{-1}).

c) Sketch the appearance of the proton and deuterium NMR spectra of molecule 1, carefully justifying the relative intensities of the transitions in each spectrum. Which spectrum would you expect to be more intense, and why?

d) Explain as fully as possible the effect on the two spectra of replacing both X substituents by chlorine atoms (^{35}Cl and ^{37}Cl both have I=3/2)

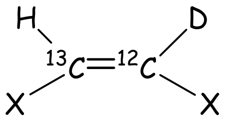
e) How and why would the proton spectrum of molecule 2 differ from that of molecule 1?



molecule 2

f) The one-bond ^{13}C-^{1}H spin-spin coupling constant in ethene is ~167 Hz. The corresponding quantities for ethane and ethyne are ~125 and ~250 Hz. Comment on these values in the context of the mechanism for spin-spin coupling.

g) Sketch the appearance of the ^{13}C NMR spectrum of molecule 3.



molecule 3

h) The spin Hamiltonian of ^{12}CHF$_2$Cl (ignoring the Zeeman interaction, the F-F spin-spin coupling, and the chlorine atom) may be written as:

$$\hat{H} = -\nu_H\hat{I}_{Hz} + J_{HF}\,(\hat{I}_{Hz}\hat{I}_{F1z} + \hat{I}_{Hz}\,\hat{I}_{F2z}\,)$$

where ν_H is the proton Larmor frequency, and J_{HF} is the H-F spin-spin coupling constant. $\hat{I}_{Hz}$, $\hat{I}_{F1z}$ and $\hat{I}_{F2z}$ are the z-components of the spin angular momentum operators of the proton and the two fluorine nuclei.

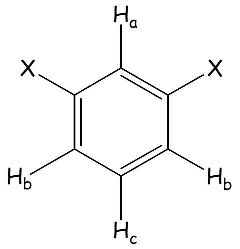
Obtain expressions for the energy levels of the HFF spin system, and the frequencies of the allowed transitions in the proton NMR spectrum, and hence demonstrate that the ^{1}H signal is a triplet.

Q3. Advanced physical chemistry 2000, Q6

Answer ALL parts.

A. *Spin-spin coupling*

a) Consider a dilute solution of the aromatic molecule shown below, in which X is an electron withdrawing group that is not magnetically coupled to the ring protons (e.g. X=Cl). Sketch the ^1H NMR spectrum if the coupling constants are in the order $J_{ortho} \gg J_{meta} \gg J_{para}$.



[Assume that the weak coupling limit applies.]

b) Explain qualitatively how the spectrum would change if

- i) the electron withdrawing groups, X, were magnetically coupled to the ring protons (e.g. X=F).
- ii) one of the X substituents were replaced by a different non-coupled electron withdrawing group, Y (e.g. Y=Br).

[Note: In part b) you are not expected to draw the NMR spectra.]

B. *Spin relaxation*

a) What is meant by *spin-lattice relaxation* and *spin-spin relaxation* in NMR? Describe the most important physical processes that give rise to each type of relaxation in solution.

b) Explain the principles behind an experiment to measure

- i) the spin-lattice relaxation time, T_1
- ii) the spin-spin relaxation time, T_2.

c) What are the experimental consequences of

- i) a very long T_1
- ii) a very short T_1.

d) An inversion recovery experiment was conducted to determine the value of T_1 for the methyl carbons in 1,2-dimethyl benzene. The intensity of the ^{13}C NMR signal is given below as a function of the pulse delay, t. $I(\infty)$ is the fully relaxed NMR intensity for $\tau \gg T_1$.

τ / s	0	5	10	15	20	25
$I(\tau)/I(\infty)$	-1.0	-0.32	0.13	0.43	0.62	0.75

Use a graphical procedure to calculate T_1 for the methyl carbons in 1,2-dimethyl benzene. [Hint: the z-magnetisation in an inversion recovery experiment recovers as

$$M_z(\tau) = M_z(\infty)\,(1 - 2e^{-\tau/T1}).\ \ ]$$